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(54) PRODUCTION OF CHLORINE DIOXIDE

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PRODUCTION OF CHLORINE DIOXIDE

ABSTRACT OF THE DISCLOSURE

Chlorine dioxide is formed by reaction between an alkali metal chlorate and hydrochloric acid in aqueous solution. The chlorine dioxide and chlorine are removed from the reaction zone by water vapor formed by evaporation of the reaction medium.

The present invention relates to the production of chlorine dioxide, and more particularly to methods of producing chlorine dioxide from hydrochloric acid.

Chlorine dioxide is known to be prepared in a variety of ways, involving the reduction of an alkali metal chlorate, generally sodium, utilizing sulphur dioxide, sulphuric acid, chromic sulphate, methanol, sodium chloride and hydrochloric acid as reducing agents. The basic reaction in all such processes is that between chlorate and chloride in the acid solution to produce chlorine dioxide, chlorine and water, in accordance with the equation:

$$HClO_3 + HCl \longrightarrow ClO_2 + \tfrac{1}{2}Cl_2 + H_2O$$

The present invention is concerned with the process of making chlorine dioxide where the reducing agent is hydrochloric acid.

The basic reactions involved are, in the case where the alkali metal is sodium:

$$(1) - NaClO_3 + 2HCl \longrightarrow ClO_2 + \tfrac{1}{2}Cl_2 + NaCl + H_2O$$

and $(2) - NaClO_3 + 6HCl \longrightarrow NaCl + 3Cl_2 + 3H_2O$

The two reactions are competing in the reaction solution and reaction (2) becomes significant in cases when there is an excess of hydrochloric acid above the stoichiometry of the equation (1). Where such an excess of hydrochloric acid exists, therefore, the quantity of chlorine dioxide produced per mole of sodium chlorate decomposed is reduced. In order to maximize chlorine dioxide production, it is preferred to operate at or near the stoichiometry of equation (1) in the feed to the reactor.

Chlorine dioxide is produced commercially from hydrochloric acid by the so-called Day-Kesting process disclosed in Canadian Patent No. 461,586 issued December 6, 1947 to Brown Company. In this process the chlorine dioxide generator consists of a plurality of, generally six, reaction vessels arranged in series. Feed liquor containing sodium chlorate,

hydrochloric acid and some sodium chloride is fed into the upper of the six reactors, from which the solution cascades by gravity through the remaining reactors. The two bottom reactors are operated at boiling temperature and the steam strips them of chlorine dioxide while the remaining hydrochloric acid is oxidized. Air is introduced into the gas stream from the last two reactors, mixes with the vapour and is bubbled countercurrently through the solution in the reactors three to six.

In accordance with the present invention, chlorine dioxide is produced from an aqueous reaction medium containing an alkali metal chlorate and hydrochloric acid contained in a reaction vessel. Water is evaporated from the reaction medium in the vessel and removes the chlorine dioxide and chlorine from the vessel.

Thus, in accordance with the present invention, the chlorine dioxide and chlorine is all produced in a single vessel and is removed from the vessel solely with the aid of steam evaporated from the aqueous reaction medium.

It has previously been proposed in Canadian Patent No. 782,574 issued April 9, 1968 to Chemech Engineering Limited, to produce chlorine dioxide and chlorine from sodium chloride and hydrochloric acid in a single reaction vessel in place of the cascade six-vessel system used in the Day-Kesting process. In the process described in the above patent, gaseous hydrogen is passed through the reaction vessel to agitate the reaction liquor and as gaseous diluent for the chlorine dioxide and chlorine.

Chlorine dioxide gas in concentrated gas form is spontaneously explosive and in processes of producing chlorine dioxide it is necessary to make some provision for diluting the gases produced in the reaction. Air has commonly been used, as in the commercial Day-Kesting operation described above,

and in the Canadian Patent No. 782,574, hydrogen is the diluent gas. The gaseous stream from the reactor used in Canadian Patent 782,574 contains water vapour in addition to the chlorine dioxide, chlorine and hydrogen.

In accordance with the present invention, steam is the sole diluent carrier gas for the gaseous reaction products. Such operation is advantageous over the hydrogen inert gas used in the above patent, since there is a danger of explosion of the gas mixture containing chlorine dioxide, chlorine and hydrogen, albeit reduced with regard to the danger of explosion where undiluted chlorine dioxide is involved, but by no means an insignificant danger. By contrast, operation in accordance with the present invention substantially eliminates the possibility of explosion.

In addition, operation in accordance with the present invention reduces the overall volume of gas to be handled, as compared to the hydrogen stripping operation described above. Further, less elaborate equipment is required in the operation of the present invention as compared with the operation described in Canadian Patent No. 782,574.

It will be apparent therefore that the present invention gives rise to considerable advantages over prior art systems of producing chlorine dioxide from sodium chlorate and hydrochloric acid.

In practice, the process of the present invention is carried out at the boiling temperature of the reaction liquor. Operating in this manner ensures maximum vapourization of water from the reaction solution in the vessel, whereby chlorine dioxide and chlorine are rapidly educted from the vessel. The temperature of the reaction solution should be below the temperature above which substantial decomposition of chlorine dioxide occurs. It is preferred to operate the reaction vessel at temperatures of approximately 60° to 80° C. In order to maintain

the reaction solution in a boiling state in this temperature range, the reaction vessel is subjected to a reduced pressure. The magnitude of the reduced pressure is dependent upon the boiling temperature required.

Any convenient equipment may be utilized to subject the reaction vessel to a reduced pressure, for example, a water jet eductor may be used. The water fed to the eductor serves not only to produce the required reduced pressure, but also to condense the water vapour and to dissolve the chlorine dioxide and part of the chlorine produced.

A variety of reaction vessels may be utilized in the practice of the present invention. A suitable one is described in Canadian Patent No. 825,084 issued October 14, 1969 to Electric Reduction Company of Canada, Limited modified as required, depending on whether or not solids are deposited in the vessel. Such Canadian Patent describes the production of chlorine dioxide from an alkali metal chlorate, an alkali metal chloride and sulphuric acid in a single vessel generator-evaporator-crystallizer.

There are significant advantages to producing chlorine dioxide from an alkali metal chlorate with hydrochloric acid in a single vessel wherein the chlorine dioxide and chlorine produced are removed from the vessel by steam, in accordance with the present invention, as opposed to producing chlorine dioxide in accordance with the process of Canadian Patent 825,084 from an alkali metal chlorate, an alkali metal chloride and sulphuric acid, again removing the chlorine dioxide and chlorine with steam.

Thus, the by-product of the sulphuric acid process is an alkali metal sulphate. Generally, such alkali metal sulphate is added to the recovery system of a Kraft mill operation to make up sulphur value losses. However, with increasing efficiency of Kraft mill recovery systems, especially in recover-

ing sulphur values, sulphate make-up requirements are falling. In some installations, an excess of sodium sulphate over requirements may be generated.

Further, the hydrochloric acid operation of the present invention can operate at very low acidities, generally below 1N, whereas the sulphuric acid operation requires acidities of at least 2N and generally around 10N. Therefore, there is less danger of corrosion to equipment by operating in accordance with the present invention.

Further, the sulphuric acid operation requires three reactants, whereas the hydrochloric acid operation utilizes two.

It is apparent that the present invention represents a considerable advance in the art over conventional hydrochloric acid-based operations and over the sulphuric acid-based single vessel operation of the above-mentioned Canadian patent.

As mentioned above, it is preferred to operate the process of the present invention at molar concentration where the ratio of Cl^- : ClO_3^- is approximately 2:1. It is possible to use lower ratios, say 1:1, but all of the chlorate present is not reacted under these circumstances. It also is possible to use higher ratios of chloride to chlorate, say 5:1, but at these concentrations, equation (2) above becomes predominant, producing large quantities of chlorine in preference to chlorine dioxide.

The acidity of the reacting solution as indicated above is generally below 1N, preferably about 0.5N. In one particularly preferred embodiment described below the acidity may drop to 0.1-0.2N. The effective range of acidities in the process of the present invention is generally 0.05 to 1N.

The quantity of water evaporated from the reacting solution may be insufficient to produce precipitation of alkali

metal chloride in the reaction vessel, but in accordance with a particularly preferred embodiment of the invention, the quantity of water evaporated is sufficient to precipitate alkali metal chloride in the reaction vessel.

The process of the present invention will be described hereinafter with reference mainly to sodium salts, but it is understood that the present invention is applicable to other alkali metal salts, such as potassium salts.

In operations where the sodium chloride is not precipitated, the effluent from the reaction vessel, containing dissolved sodium chloride in addition to unreacted sodium chlorate and hydrochloric acid, may be fed to a chlorate cell wherein the sodium chloride is converted to sodium chlorate and hydrogen by electrolysis. The solution enriched with respect to sodium chlorate then is returned to the reaction vessel. The hydrochloric acid contained in the spent reaction liquor fed to the cell is decomposed in the cell.

Alternatively, the spent reaction liquor may be further evaporated or subjected to cooling to precipitate the sodium chloride. The mother liquor then may be recycled directly to the reaction vessel.

It is preferred to produce the chlorine dioxide and chlorine continuously by continuously feeding an aqueous solution of sodium chlorate and continuously feeding a separate stream of hydrochloric acid to a reaction vessel subjected to reduced pressure and containing boiling reaction liquid, and continuously removing chlorine dioxide, chlorine and water vapour from the reaction vessel.

Where no sodium chloride is precipitated, reaction liquor is continuously removed from the vessel, to maintain the level of liquid within the vessel at a substantially constant level, and is continuously fed to a chlorate cell. The chlorate cell continuously subjects fed liquor to electrolysis to

generate a liquid effluent rich in sodium chlorate and a gaseous effluent consisting substantially of hydrogen. The liquid effluent from the cell is continuously fed to the reaction vessel as the sodium chlorate feed stream.

The embodiment of the invention wherein sodium chloride is precipitated now is described.

In accordance with this particularly preferred embodiment of the invention, sufficient water is evaporated from the reaction liquor within the vessel, that sodium chloride is precipitated in the vessel. This may be induced by feeding substantially concentrated solutions of sodium chlorate and hydrochloric acid to the reaction vessel. Upon reaction between the sodium chlorate and the hydrochloric acid and upon evaporation of water, sodium chloride precipitates out of the reaction liquor in the vessel. The vessel, therefore, may operate as a single vessel generator-evaporator-crystallizer.

It further has been found that it is possible to operate the process at extremely low acidities of the order of 0.1 to 0.2N and precipitate sodium chloride from the solution. The acidity of the reaction solution will attain a steady state when the process is operated continuously. The acidity of the reaction medium will depend upon a number of factors such as initial concentration of feeds, temperature and quantity of water evaporated off.

Some spent reaction liquor may overflow from the reaction vessel and is recycled to the make-up feed streams. The precipitated crystalline sodium chloride is removed from the reaction vessel and washed with water to remove last traces of trapped reaction medium. The spent wash water may be fed along with the recycled reaction medium to the reaction vessel.

The sodium chloride thereby is recovered in a substantially pure state. It may be put to a variety of uses. It is

preferred, however, to dissolve the sodium chloride in water and feed the aqueous solution to the chlorate cell preparing the sodium chlorate feed for the reaction vessel. Sodium chloride recovered by crystallization from spent reaction liquor outside the vessel similarly may be used to prepare sodium chloride solution for feed to the chlorate cell.

It is preferred to feed fresh sodium chloride solution to the chlorate cell rather than spent reaction liquor containing dissolved sodium chloride, as in the case described above where sodium chloride is not precipitated.

The spent reaction liquor contains besides sodium chloride unreacted sodium chlorate and hydrochloric acid and also dissolved chlorine dioxide and chlorine not stripped in the reaction vessel. The presence of these materials gives rise to a series of side reactions, some potentially dangerous with large quantities of hydrogen mixing with the chlorine dioxide and chlorine, which side reactions reduce the efficiency of the cell in its conversion of sodium chloride into sodium chlorate.

In contrast, where the feed is sodium chloride solution prepared from precipitated sodium chloride, the solution is substantially free from impurities, and therefore side reactions are substantially diminished. Therefore, operation of the process to precipitate sodium chloride in the reaction vessel is preferred to operations wherein the sodium chloride remains dissolved in the solution.

It is preferred to operate continuously the process in which sodium chloride is precipitated. Thus, an aqueous solution of sodium chlorate and a separate stream of hydrochloric acid are continuously fed to a reaction vessel subjected to a reduced pressure and containing boiling reaction liquid. Chlorine dioxide, chlorine and water vapour are continuously removed from the reaction vessel and sodium chloride is continuously precipitated in the reaction vessel. Overflow spent reaction

liquor may be continuously removed from the reaction vessel and make-up sodium chlorate solution continuously added thereto, and the overflow spent liquor together with make-up sodium chlorate solution are continuously fed to the reaction vessel as the sodium chlorate stream. Sodium chloride is continuously removed from the reaction vessel, continuously dissolved in water and continuously fed to a chlorate cell wherein it is converted into sodium chlorate and hydrogen.

The sodium chlorate is continuously fed to the reaction vessel as make-up chlorate feed.

In operations where the sodium chlorate feed stream is prepared from purchased sodium chlorate, it may be desirable to sell the precipitated sodium chloride,there being a ready market for this material.

In many bleaching operations involving bleaching with chlorine and chlorine dioxide, the pulp after each bleaching step is subjected to caustic extraction with sodium hydroxide solution. The sodium hydroxide solution often is prepared on site by electrolysis of sodium chloride solution in a caustic cell. The sodium chloride recovered from the reaction vessel therefore could be used to prepare the feed solution for the caustic cell.

The hydrochloric acid feed for the reaction vessel operating in accordance with the present invention may be purchased as such, prepared from purchased hydrogen chloride gas, or preferably formed by combusting purchased chlorine with hydrogen off-gas from a chlorate cell and then dissolving the hydrogen chloride in water. In some operations it may be desirable to feed hydrogen chloride gas directly into the reaction vessel.

Some of the chlorine used to combust with the hydrogen may be supplied by chlorine generated in the reaction vessel.

The reaction occurring in the chlorate cell is:

$$NaCl + 3H_2O \longrightarrow NaClO_3 + 3H_2$$

and the reaction involved in producing hydrogen chloride by combustion is:

$$H_2 + Cl_2 \longrightarrow 2HCl$$

It will be seen from the above equation 1 that only two moles of hydrogen chloride (as hydrochloric acid in the reaction medium) is required for each mole of sodium chlorate. Therefore, only one-third of the mole quantity of hydrogen produced in the chlorate cell need be combusted with one mole of chlorine to produce the required mole amount of hydrogen chloride, and therefore ultimately the required mole amount of hydrochloric acid.

The excess hydrogen may be burned in air or oxygen to produce heat which enables the heat balance of the operation to be maintained, and water which may be used as part of the water requirement.

Wholly integrated systems therefore may be provided in accordance with the present invention in which the only feed stocks are chlorine and water and the only effluent is chlorine dioxide solution. Such integrated systems may be provided for both the case where sodium chloride is not precipitated and the case where sodium chloride is precipitated.

The present invention is further described by way of example with reference to the accompanying drawings, in which:

Figure 1 represents a flow sheet for an integrated system in accordance with one embodiment of the present invention;

Figure 2 represents a flow sheet for an integrated system in accordance with another embodiment of the present invention; and

Figure 3 represents a flow sheet for an integrated system in accordance with another embodiment of the present invention.

Referring to Figure 1, a chlorine dioxide generator 10, such as one described in above-mentioned Canadian Patent 825,084, containing a boiling aqueous reaction medium of sodium chlorate and hydrochloric acid is fed by sodium chlorate solution from a chlorate cell 12 through line 14. Hydrochloric acid is fed to the generator 10 through line 16 from hydrogen chloride absorber 18. The generator 10 is maintained under reduced pressure. Typical reaction conditions are 60°C at 150-200mm Hg.

The feeds are maintained at such a rate and the reactor liquor of sufficient concentration that product sodium chloride does not precipitate out. The level of reaction liquid is maintained substantially constant by adjusting the rates of the feed streams, the rate of removal of liquid as overflow, and the rate of removal of water by evaporation.

Overflow liquor from the reactor, containing sodium chloride, unreacted sodium chlorate and hydrochloric acid, and dissolved chlorine dioxide and chlorine is fed through line 20 to the cell 12. The liquor is electrolysed within the cell 12, converting the sodium chloride to sodium chlorate and converting the hydrochloric acid to hydrogen and chlorine. The effluent of the cell 12 is a liquid substantially enriched with sodium chlorate and containing some unconverted sodium chloride. This liquid is fed to the generator 10 through line 14.

The gaseous products of the cell 12, consisting mainly of hydrogen but containing a small amount of chlorine from the decomposition of the hydrochloric acid are fed by line 22 to a hydrogen chloride burner 24. Chlorine from a source of chlorine (not shown) is fed through lines 26 and 28 to the burner 24 and part of the hydrogen burns both with the chlorine fed to the burner 24 through line 28 and also with the chlorine in the off-gases from the cell 12 to produce hydrogen chloride. The burner 24 may be replaced by a fuel cell and the hydrogen and chlorine could be reacted therein, recovering electric power.

The hydrogen chloride gas, together with unreacted hydrogen, passes through line 30 to the absorber 18. Water is fed to the absorber 18 through line 32 to dissolve the incoming hydrogen chloride to produce hydrochloric acid. It may be desired in certain operations to feed the hydrogen chloride gas directly from the burner to the reaction vessel.

The excess unreacted hydrogen passes out of the absorber through line 34, generally for combustion with oxygen to produce water and heat. Alternatively, the hydrogen may be reacted with oxygen in a fuel cell thereby generating electric power.

The hydrochloric acid formed in the absorber 18 then is fed by line 16 to the generator 10. The gaseous products of the generator 10, i.e. chlorine dioxide, chlorine and steam, are fed by line 36 to a chlorine dioxide absorber 38. Water is fed by line 40 to the absorber 38 to absorb chlorine dioxide from the gaseous products and to condense the steam. The water fed by line 40 may be the feed of a water eductor used to maintain the generator 10 under reduced pressure.

The vacuum may be produced in any convenient manner such as a liquid venturi fed with recycled chlorine water formed by condensation of remaining water vapour and dissolving of part of the chlorine by this water. Alternatively, the vacuum may be provided by a pump attached to the gas outlet of the absorber 38. The pump discharges a mixture of gaseous chlorine and aqueous chlorine which can be held in a tank, and the chlorine solution recycled to the pump. It may be necessary from time to time to remove some of the chlorine water. Such chlorine water can be readily utilized in the bleaching plant.

An aqueous solution of chlorine dioxide, containing some dissolved chlorine, is recovered through line 42 and is suitable as feed for a chlorine dioxide bleaching installation.

Undissolved chlorine passes out of the absorber through line 44 to augment the chlorine gas feed through line 28 to the burner 24.

It will be understood that, for the sake of simplicity, pumps and hold tanks have been omitted.

Turning now to consideration of the embodiment of Figure 2, a generator 110, such as the one disclosed in the abovementioned Canadian Patent No. 825,084, containing a boiling aqueous reaction medium of sodium chlorate and hydrochloric acid and maintained under a reduced pressure is fed with sodium chlorate solution by lines 112 and 114. Hydrochloric acid from a hydrogen chloride absorber 116 is fed through line 118. The generator 110 evaporates sufficient water from the reaction medium that sodium chloride is precipitated out in the generator. It is preferred that the evaporation be sufficient to maintain the level of reaction liquor in the vessel 10 at a substantially constant level. Any overflow liquor from the reactor containing unreacted sodium chlorate and hydrochloric acid is recycled through line 120 to the sodium chlorate feed stream 114.

The rate of feed of reactants, the rate of removal of liquid as overflow, and rate of evaporation of water, are maintained at such a value that the level of reaction medium within the generator remains substantially constant.

Sodium chloride deposited in the generator 110 is removed through line 122 to a separator/washer 124. The sodium chloride crystals are separated from reaction liquor and are washed. The spent wash water and separated reaction liquor may be passed to waste or, as illustrated in Figure 2, fed to the generator 110 by lines 128, 120 and 114.

The washed substantially pure crystals of sodium chloride next are passed to a dissolver 130 by line 132. Water fed

through line 134 dissolves the sodium chloride in the dissolver 130 to form an aqueous solution of sodium chloride. The aqueous
3 solution of sodium chloride so formed is fed by

line 136 to a chlorate cell 138. The sodium chloride is electrolysed in the chlorate cell 138 to form a sodium chlorate solution and hydrogen. The sodium chlorate solution is fed through lines 112 and 114 to the generator 110.

The off-gas from the chlorate cell 138, consisting essentially of hydrogen, is fed by line 140 to a hydrogen chloride burner 142. Chlorine is fed from a source of chlorine (not shown) through lines 144 and 146 to the burner. Chlorine fed through line 146 to the burner 142 is burned in part of the hydrogen and the hydrogen chloride produced, together with unreacted hydrogen, is fed through line 148 to hydrogen chloride absorber 116.

Alternatively, the burner may be replaced by a fuel cell to which the hydrogen and chlorine are fed, hydrogen chloride is produced and electric power is also produced.

Water is fed through line 150 to the absorber 116 to dissolve the hydrogen chloride to provide hydrochloric acid of the desired concentration. Excess hydrogen passes through line 152.

It may be desirable under some circumstances to feed hydrogen chloride gas directly to the generator.

The excess hydrogen may be burned with oxygen to produce heat, to balance the energy values, and water, which may be used as part of the requirement of the system. Alternatively, the hydrogen and oxygen may be fed to a fuel cell and electrical energy recovered thereby.

The hydrochloric acid produced in the absorber 116 is passed through line 118 to the generator 110. The gaseous products of the generator 110 consisting essentially of chlorine dioxide, chlorine and steam, are passed by line 154 to a chlorine dioxide absorber 156.

Water is fed to the absorber 156 through line 158 to condense at least part of the water vapour and to dissolve the

chlorine dioxide. The liquid effluent of the absorber 156 leaving through line 160 is an aqueous solution of chlorine dioxide, containing some dissolved chlorine and is suitable for use as feed for a chlorine dioxide bleaching operation.

The water fed through line 158 may be used as feed for a water eductor which maintains the generator 110 at the desired reduced pressure.

Chlorine gas from the absorber 156 is fed by line 162 to the chlorine feed stream 146 to the hydrogen chloride burner 142.

The means imparting the reduced pressure to the generator 110 may be located in the chlorine line 162 near the exit of the absorber 156. Such means may take the form of a pump or a liquid fed venturi. In such a system, a certain amount of water vapour is drawn into the pump or venturi, together with the chlorine. Upon condensation, chlorine water is provided as well as chlorine gas. The gas is fed along line 162 and the water is recycled to the pump or venturi to contact incoming chlorine and water vapour. If the chlorine water accumulates excessively, it may be necessary from time to time to remove part of this chlorine water. Such removed chlorine water may be used in a bleach plant.

It will be understood that for the sake of simplicity pumps and hold tanks have been omitted.

The present invention therefore provides continuous integrated systems of producing chlorine dioxide solution as the only effluent with the only feed streams required being chlorine and water.

The heat generated by the chlorate cells may be utilized as part of the heat requirement of the generators by use of heat exchangers. Heat also may be imparted to the generator by combusting the excess hydrogen with oxygen.

A number of modifications clearly are possible to the

above-described integrated systems as will be obvious to anyone skilled in the art.

For example, the hydrogen chloride required could be obtained by reacting sodium chloride with sulphuric acid. Further, the chlorine dioxide production facility could be separated from the chlorate producing unit. In such an operation, chlorine would be recovered as chlorine water for use in the mill rather than as gas for production of hydrogen chloride as described above. Such operation further requires the shipping of hydrochloric acid or hydrogen chloride and dry chlorate to the mill with sodium chloride being returned to the chlorate plant.

In another modification, dry sodium chlorate from a chlorate plant could be shipped to the mill and exchanged by metathesis for sodium chloride, which then is returned to the chlorate plant for re-use. In such an operation, purchased hydrogen would be required to burn with the chlorine.

A still further modification contemplates association of the pulp mill with a caustic cell. The chlorine dioxide generator may be operated with purchased chlorine and chlorine and hydrogen obtained from the caustic cell may be used to generate the hydrochloric acid. The sodium chloride recovered from the generator could be used in the caustic cell.

In many pulp mill installations, the chlorine dioxide generator is sulphuric acid based, thereby producing sodium sulphate as by-product. Such sodium sulphate is used as make-up for sulphur and sodium values in the conventional recovery operations in which the black liquor from the digestion of the pulp with white liquor containing sodium sulphide and sodium hydroxide, is concentrated and sodium sulphate is added to the concentrated liquor prior to burning in a furnace. The smelt is dissolved in water, and the resulting green liquor causticized with lime to precipitate calcium carbonate to regenerate the

white liquor. As indicated above, with increasing recovery of sodium and sulphur values from the flue of the furnace, the quantity of sodium sulphate required as make-up falls. A chlorine dioxide generator, therefore, may produce more by-product sodium sulphate than is required in the Kraft mill.

The present invention provides a method of production of chlorine dioxide which increases the chlorine dioxide capacity while decreasing the sodium sulphate output.

A single vessel chlorine dioxide generator based on hydrochloric acid, as disclosed above, may be used in conjunction with an existing chlorine dioxide generator based on sulphuric acid.

Sulphuric acid-based systems involve the following reactions

1. $MClO_3 + MCl + H_2SO_4 \longrightarrow ClO_2 + \frac{1}{2}Cl_2 + M_2SO_4 + H_2O$

2. $MClO_3 + 5MCl + 3H_2SO_4 \longrightarrow 3Cl_2 + 3M_2SO_4 + 3H_2O$

where M is an alkali metal. The equation 2 becomes significant when the mole ratio of chloride to chlorate exceeds 1:1. Since no chlorine dioxide is produced by the process of equation 2, to maximize production of chlorine dioxide, it is preferred to operate at an approximately equimolar ratio of chlorate to chloride in the feed to the reactor.

A method of operating a sulphuric acid-based generation system used commercially is known as the "Rapson R2" process, also known as the "Hooker-R2" and "ER2" processes. This process is disclosed in Canadian Patent No. 543,589 issued July 16, 1957 to Electric Reduction Company of Canada, Limited and involves introduction into a generator of a stream of an aqueous solution of approximately equimolar proportions of an alkali metal chlorate and an alkali metal chloride and a stream of concentrated sulphuric acid. Air is introduced at the bottom of the generator to carry chlorine dioxide and chlorine produced in the generator out of the generator to further

processing to separate the chlorine dioxide from the chlorine. The aqueous effluent of the generator contains an alkali metal bisulphate and unreacted alkali metal chlorate, alkali metal chloride and sulphuric acid. The bisulphate may be crystallized and the mother liquor returned to the generator. The alkali metal is generally sodium.

The R2 process generally is carried out under conditions of high acidity, usually about 10N. In accordance with an invention described in Canadian Patent 826,517 issued November 4, 1969 to Electric Reduction Company of Canada, Limited, chlorine dioxide and chlorine can be obtained by reacting sodium chlorate, sodium chloride and sulphuric acid under conditions of low acidity, generally of the order of 2 to 4.8N. The effluent from the generator in this case contains sodium sulphate (Na_2SO_4) in addition to unreacted sodium chlorate, sodium chloride and sulphuric acid. The sodium sulphate may be recovered either by evaporating the solution, in which case the sodium sulphate is recovered as anhydrous sodium sulphate, or by cooling the solution, in which case the sodium sulphate is recovered as sodium sulphate decahydrate ($Na_2SO_4.10H_2O$). The mother liquor then is recycled to the generator.

In the above-mentioned Canadian Patent No. 825,084, there is described a process of forming chlorine dioxide and chlorine from an alkali metal chlorate, alkali metal chloride and sulphuric acid, in which chlorine dioxide and chlorine are generated and an alkali metal sulphate crystallized in the same vessel. This may be achieved by operating the generator at the boiling point of the reactants under reduced pressure. The water evaporated thereby serves to remove the chlorine dioxide and chlorine from the vessel.

The alkali metal sulphate is recovered from the vessel

and the reaction liquor recycled to the generator inlet.

The alkali metal is generally sodium. The form of sodium sulphate produced is dependent on the acidity of the reacting liquor. At high acidities around 10 to 12N, the sodium sulphate is in the form of sodium bisulphate ($NaHSO_4$) whereas at acidities around 5 to 6N the sodium sulphate is in the form of sodium sesquisulphate ($Na_3H(SO_4)_2$) or a mixture of sodium bisulphate with sodium sesquisulphate.

The process disclosed in Canadian Patent No. 826,577 is preferably performed in a single vessel generator-evaporator-crystallizer wherein the weakly acid solution is reacted at the boiling point of the solution under reduced pressure. The water vapour removes the chlorine dioxide and chlorine from the vessel. Under the conditions of low acidity, i.e. about 2 to 4.8N, the sodium sulphate deposited is generally anhydrous sodium sulphate (Na_2SO_4), possibly mixed with some sodium sesquisulphate at the high end of the acidity range.

The sulphuric acid-based systems will be described hereinafter with respect to sodium chlorate and sodium chloride as feeds, but it is understood that sulphuric acid systems, with the exception of the low acidity system described in Canadian Patent No. 826,577 which is limited to sodium materials, may be operated with other alkali metal salts.

The hydrochloric acid-based system of the present invention may be combined with any of the above-described sulphuric acid systems in a variety of ways.

One such combination is illustrated in Figure 3. A chlorine dioxide generator 210, such as the one described in Canadian Patent No. 825,084, contains a boiling aqueous reaction medium of sodium chlorate and hydrochloric acid. The generator is maintained under a reduced pressure. A concentrated solution of sodium chlorate is fed to the generator

210 through line 212 from a chlorate concentrator 214. Hydrogen chloride, or hydrochloric acid, if desired, is fed to generator 210 through line 216 from hydrogen chloride burner 218.

A chlorate cell 220 produces sodium chlorate solution by electrolysis of sodium chloride solution fed through line 222 from a sodium chloride dissolver 224. Sodium chloride is fed to the dissolver 224 through line 226 and water is fed to the dissolver through line 228.

Liquid effluent from the chlorate cell consisting of sodium chlorate and unreacted sodium chloride leaves the cell through line 230. Part of the effluent is fed through line 232 to the concentrator 214. The solution is concentrated to precipitate some sodium chloride and to provide a concentrated sodium chlorate solution. The sodium chloride is recycled to the dissolver 224 through line 234, and the sodium chlorate solution fed to the generator 210 through line 212.

Gaseous products of the chlorate cell, consisting substantially of hydrogen, leave the cell through line 236. Two-thirds of the mole amount of hydrogen leaves the system through line 238 for further utilization, such as to be burned with oxygen to produce heat which can be utilized as part of the heat requirement of the system, or to be fed to a fuel cell also fed with oxygen, to thereby generate electrical energy.

The remaining one-third of the mole quantity of hydrogen is fed to the hydrogen chloride burner 218. Chlorine is fed to the burner through lines 240 and 242. The chlorine burns with the hydrogen to produce hydrogen chloride which is fed as such, as hydrochloric acid after absorption in water, through line 216 to the generator 210.

The liquid level in the generator 210 is maintained substantially constant by adjusting appropriately feed rates and evaporation rates. Overflow liquor from the generator, consisting of unreacted sodium chlorate and hydrochloric acid, is

recycled through line 244 to the sodium chlorate feed stream 212.

The sodium chlorate- and sodium chloride-containing effluent from the cell 220 is partially fed through line 246 to a chlorine dioxide generator 248. Generator 248, such as the one described in Canadian Patent No. 825,084, contains a boiling aqueous reaction mixture of sodium chlorate, sodium chloride and sulphuric acid. The generator 248 is maintained under a reduced pressure. Sulphuric acid is fed to the reaction mixture through line 250. The level of the reaction mixture is maintained substantially constant within the generator 248 by appropriate adjustment of flow rates and rate of evaporation of water and overflow liquid containing unreacted sodium chlorate, sodium chloride and sulphuric acid is recycled to the sodium chlorate feed stream 246 through lines 252 and 254.

In the generator 210, sodium chloride is crystallized out of the reaction medium. This sodium chloride is fed through lines 256 and 254 to the sodium chlorate feed stream 246 of the generator 248. The sodium chloride product of the hydrochloric acid-based generator 210 is used as the sodium chloride feed for the sulphuric acid-based generator 248.

Sodium sulphate is crystallized out of the reaction medium in the generator 248 and exits through line 258, generally for feed to the Kraft mill recovery operation. The form of the sodium sulphate will depend upon the acidity of the reaction medium, as indicated above.

Gaseous products of generator 210, consisting of chlorine dioxide, chlorine and water vapour, are fed through lines 260 and 262 to a chlorine dioxide absorber 264. Gaseous products of generator 248, consisting of chlorine dioxide, chlorine and water vapour, pass out of the generator 248 through line 266 and are fed to the chlorine dioxide absorber

264 through line 262.

Water is fed to the chlorine dioxide absorber 264 through line 268. The water serves to dissolve the chlorine dioxide and part of the chlorine and to condense a substantial part of the steam. The liquid effluent, consisting of an aqueous solution of chlorine dioxide containing some chlorine, passes out of the absorber through line 270. The chlorine dioxide solution may be fed to the bleaching plant of the mill.

Undissolved chlorine and remaining water vapour pass out of the absorber 264 through line 272 to a vacuum inducing device 274. The vacuum inducing device may be of any convenient construction, such as a venturi tube or a rotary pump.

The chlorine and remaining water vapour are contacted with recycled chlorine water fed through line 276 to the vacuum inducing device 274. The remaining water vapour thereby is condensed and the liquid products, together with gaseous chlorine, pass through line 278 to a separator 280. The gaseous chlorine is vented from the separator 280 through line 282 to the chlorine feed line 242 of the hydrogen chloride burner 218. The liquid in the separator 280 is recycled through line 276 to vacuum inducing device 274.

Chlorine water may be tapped from the separator 282 from time to time if the accumulation in separator 282 becomes too large and utilized in the bleaching plant of the mill.

It can be seen therefore that the present invention provides an integrated system for the production of chlorine dioxide from both hydrochloric acid- and sulphuric acid-based systems in which the only stock materials required are sodium chloride, chlorine and sulphuric acid and the only effluents are chlorine dioxide solution, which is utilized in the bleaching plant and sodium sulphate, which is utilized in the Kraft recovery system. Chlorine water also may form part of the effluents from time to time.

It can be seen that the quantity of sodium sulphate produced is halved for the same quantity of chlorine dioxide, as compared to the conventional sulphuric acid-based operation.

It is not necessary that the chlorine dioxide be produced in the ratio 50:50 from each generator. It is possible to vary the ratio, depending on the quantity of sodium sulphate required in the Kraft mill recovery system. Thus, if more sodium sulphate is required than is produced by the operation as described above with reference to Figure 3, then more chlorate is fed through line 246 than is fed through line 232. More sodium chloride will be required by generator 248 than would be supplied by generator 210 and a separate supply line would be necessary.

Alternatively, if less sodium sulphate is required, the proportion of the chlorate effluent from the cell 220 fed through line 232 is increased. This will give rise to an excess of sodium chloride produced in generator 210 over the requirement of the generator 248. The excess can be simply recycled to the sodium chloride feed line 226.

The sulphuric acid generator 248 may be a standard Rapson R2 generator, in place of the single vessel generator-evaporator-crystallizer 248. An air line is necessary in this modification to remove the chlorine dioxide and chlorine. Facility for crystallizing the sodium sulphate also is required.

Further, the generator 210 may be operated without deposition of sodium chloride. The whole of the liquid overflow from the generator, containing sodium chloride as well as unreacted sodium chlorate and hydrochloric acid, is fed to the generator 248 in this modification. Appropriate amounts of sodium chlorate are necessary to attempt to maintain the chlorate: chloride ratio at approximately 1:1, the chloride content being measured as including chloride from both sodium chloride and the hydrochloric acid.

It is possible to operate the system described above with reference to Figure 3 with purchased sodium chlorate and purchased hydrogen chloride. Alternatively, where sodium chlorate is purchased, and thus no hydrogen is available as by-product, hydrogen may be purchased along with chlorine to combust together on site. The hydrogen and chlorine may be reacted together in a fuel cell in place of the burner 218, thereby recovering electrical energy. Where a chlorate cell is provided, it may be more practicable under certain circumstances to use purchased hydrogen chloride and burn all of the hydrogen off-gas from the chlorate cell in oxygen and use the heat generated in the system.

The chlorine dioxide produced by the process of the present invention may be used in bleaching operations wherein a pulp of cellulosic fibrous materials is contacted with aqueous chlorine dioxide or an aqueous solution containing chlorine dioxide and chlorine.

The present invention is illustrated further by the following Examples.

EXAMPLE 1

A single vessel generator-evaporator contained a reacting solution of sodium chlorate, sodium chloride and hydrochloric acid. The solution was maintained at about 50°C and the vessel under 26 inches Hg vacuum. Effluent liquor from the vessel contained 300g/l sodium chlorate, 177g/l sodium chloride and 0.2NHCl.

The liquor fed to the vessel was a 20ml/min feed of a solution containing 350g/l sodium chlorate and 150g/l sodium chloride and a 2ml/min feed of 30% hydrochloric acid to maintain the acidity.

Chlorine dioxide and chlorine were produced in the vessel and removed by steam. The vapors were passed to an absorption system where the steam was condensed and the chlorine dioxide and chlorine separated by known methods. Chlorine dioxide was recovered from the vessel at a rate of 0.52g/min (about 38 G.A.% chlorine as chlorine dioxide) and steam was removed from the vessel at a rate of 2.5 ml/min.

The effluent liquor from the vessel was passed to an electrolytic chlorate cell operating at 35°C and 0.5 amps/sq.in. current density. The hydrochloric acid in the cell feed served to maintain the cell liquor pH at 5.1 to 5.3. The cell, operating at about 85% current efficiency, generated a liquor containing 350g/l sodium chlorate and 150g/l sodium chloride. This latter liquor constituted the feed for the vessel. Hydrogen together with about 3 to 4% chlorine was generated by the cell.

EXAMPLE 2

The procedure of Example 1 was repeated under varying single vessel generator-evaporator conditions. In each case a mixture of chlorine dioxide and chlorine was recovered. The following Table I reproduces the results:

Table I

Vessel Temp. °C	Cl^-/ClO_3^- mol ratio in feed	Acidity of reacting liquor	GA% Clas ClO_2	H_2O/ClO_2 Wt. ratio in vapors
55	0.68	0.17	39-40	8.9
55	0.70	0.20	38-39	5.2
60	0.50	0.12	40-41	7.8
70	0.47	0.07	39-40	7.4

Modifications are possible within the scope of the invention.

THE EMBODIMENTS OF THE INVENTION IN WHICH AN EXCLUSIVE PROPERTY OR PRIVILEGE IS CLAIMED ARE DEFINED AS FOLLOWS:

1. A process for the production of chlorine dioxide which comprises forming an aqueous reaction medium containing an alkali metal chlorate and hydrochloric acid in a reaction zone and having an acidity of about 0.05 to about 1N by feeding to said reaction zone hydrochloric acid and an aqueous solution of said alkali metal chlorate, heating said aqueous reaction medium to effect reaction between said alkali metal chlorate and hydrochloric acid to generate thereby chlorine dioxide and chlorine and to evaporate water from said medium, and removing said chlorine dioxide and chlorine from said reaction zone as a gaseous mixture consisting of said chlorine dioxide and chlorine and said evaporated water.

2. The process of claim 1 wherein said reaction zone is maintained under reduced pressure and said aqueous reaction medium is substantially at its boiling temperature.

3. A process for the production of chlorine dioxide which comprises continuously forming in a reaction zone an aqueous reaction medium containing an alkali metal chlorate and hydrochloric acid and having an acidity of about 0.05 to about 1N by feeding separately to said reaction zone hydrochloric acid and an aqueous solution of said alkali metal chlorate, continuously forming chlorine dioxide and chlorine by reaction between said alkali metal chlorate and said hydrochloric acid in said reaction medium, continuously evaporating water from said aqueous medium to form continuously a gaseous phase in said reaction zone consisting of a mixture of chlorine dioxide, chlorine and water vapor, continu-

ously conducting said mixture out of said reaction zone, continuously recovering chlorine dioxide from said mixture, and continuously withdrawing from said aqueous reaction medium an aqueous solution containing alkali metal chloride and unreacted alkali metal chlorate and hydrochloric acid.

4. The process of claim 3 wherein said alkali metal chlorate is sodium chlorate.

5. The process of claim 3 wherein said reaction zone is continuously subjected to a reduced pressure and said reaction medium is continuously maintained substantially at its boiling temperature.

6. The process of claim 3 including the steps of continuously electrolyzing said aqueous solution containing alkali metal chloride to convert said alkali metal chloride at least partially to alkali metal chlorate, and continuously feeding the alkali metal chlorate-containing solution to said reaction zone.

7. The process of claim 6 wherein said electrolyzing continuously generates hydrogen gas and including the steps of continuously reacting at least part of said hydrogen gas, with chlorine gas to generate hydrogen chloride, continuously forming hydrochloric acid from said hydrogen chloride and continuously feeding at least part of said hydrochloric acid to said reaction zone.

8. A process for the production of chlorine dioxide which comprises continuously forming in a reaction zone an aqueous reaction medium containing an alkali metal chlorate and hydrochloric acid and having an acidity of about 0.05 to about 1N by

feeding separately to said reaction zone hydrochloric acid and an aqueous solution of said alkali metal chlorate continuously forming chlorine dioxide and chlorine by reaction between said alkali metal chlorate and said hydrochloric acid in said reaction medium, continuously evaporating water from said aqueous medium to form a gaseous phase in said reaction zone consisting of a mixture of chlorine dioxide, chlorine and water vapor and to deposit alkali metal chloride in said reaction zone, continuously conducting said mixture out of said reaction zone, continuously recovering chlorine dioxide from said mixture, and removing deposited alkali metal chloride from said reaction zone.

9. The process of claim 8 wherein said alkali metal chlorate is sodium chlorate.

10. The process of claim 8 wherein said reaction zone is continuously subjected to a reduced pressure and said reaction medium is continuously maintained substantially at its boiling temperature.

11. The process of claim 8 including the steps of forming an aqueous solution from said deposited alkali metal chloride, continuously electrolyzing said latter aqueous solution to convert the alkali metal chloride at least partially to alkali metal chlorate, and continuously feeding the alkali metal chlorate-containing solution to said reaction zone.

12. The process of claim 11 wherein said electrolyzing continuously generates hydrogen gas, and including the steps of continuously reacting at least part of said hydrogen gas with chlorine gas to generate hydrogen chloride, continuously forming

hydrochloric acid from said hydrogen chloride and continuously feeding at least part of said hydrochloric acid to said reaction zone.

13. A process for the production of chlorine dioxide which comprises forming an aqueous reaction medium containing sodium chlorate and hydrochloric acid and having an acidity of about 0.05 to about 1N in a first reaction zone by feeding to said first reaction zone hydrochloric acid and an aqueous solution of said sodium chlorate, heating said aqueous reaction medium to effect reaction between said sodium chlorate and hydrochloric acid to generate thereby chlorine dioxide and chlorine, to evaporate water from said medium and to deposit sodium chloride in said first reaction zone, removing said chlorine dioxide and chlorine from said first reaction zone as a gaseous mixture consisting of said chlorine dioxide and chlorine and said evaporated water, forming an aqueous reaction medium containing sodium chlorate, at least part of the deposited sodium chloride and sulphuric acid in a second reaction zone, heating said latter aqueous reaction medium to effect reaction between said sodium chlorate, sodium chloride and sulphuric acid to generate thereby chlorine dioxide and chlorine, to evaporate water from said latter medium and to form a sodium sulphate, removing said chlorine dioxide and chlorine from said second reaction zone as a gaseous mixture consisting of said chlorine dioxide and chlorine and said evaporated water, and recovering said chlorine dioxide from said gaseous mixtures.

14. The process of claim 13 wherein each of said first and second reaction zones is subjected to a reduced pressure and each of said reaction mediums is maintained substantially at its

boiling temperature.

15. A process for the production of chlorine dioxide which comprises forming a first aqueous reaction medium containing sodium chlorate and hydrochloric acid and having an acidity of about 0.05 to about 1N in a first reaction zone by feeding to said first reaction zone hydrochloric acid and an aqueous solution of said alkali metal chlorate, heating said aqueous reaction medium to effect reaction between said sodium chlorate and hydrochloric acid to generate thereby chlorine dioxide and chlorine and to evaporate water from said medium, removing said chlorine dioxide and chlorine from said first reaction zone as a gaseous mixture consisting of said chlorine dioxide and chlorine and said evaporated water, recovering by-product sodium chloride from said reaction zone, forming a second aqueous reaction medium in a second reaction zone, said second reaction medium containing sodium chlorate, sodium chloride and sulphuric acid, at least part of said latter sodium chloride being provided by said recovered by-product sodium chloride, generating chlorine dioxide and chlorine from said second reaction medium, recovering said latter chlorine dioxide and chlorine from said second reaction zone, and recovering chlorine dioxide from the gaseous mixtures removed from said first and second reaction zones.

16. The process of claim 15 wherein said first aqueous reaction medium is heated to effect reaction between said sodium chlorate and hydrochloric acid to generate thereby chlorine dioxide and chlorine, to evaporate water from said medium and to deposit sodium chloride in said first reaction zone, and said deposited sodium chloride is recovered from said first reaction

zone as said by-product sodium chloride.

17. The process of claim 15 wherein said chlorine dioxide and chlorine generated in said second reaction zone is removed therein in gaseous admixture with an inert gas.

18. The process of claim 13 wherein the aqueous reaction medium in said second reaction zone has an acidity of from about 2 to about 4.8N.

19. The process of claim 9 wherein said aqueous reaction medium has an acidity of about 0.1 to about 0.2N.

20. The process of claim 8 wherein said reaction zone is continuously subjected to a reduced pressure, said reaction medium is continuously maintained substantially at its boiling temperature, said alkali metal chlorate is sodium chlorate and said aqueous reaction medium has an acidity of about 0.1 to about 0.2N.

21. The process of claim 13 wherein said aqueous reaction medium has an acidity of about 0.1 to about 0.2N.

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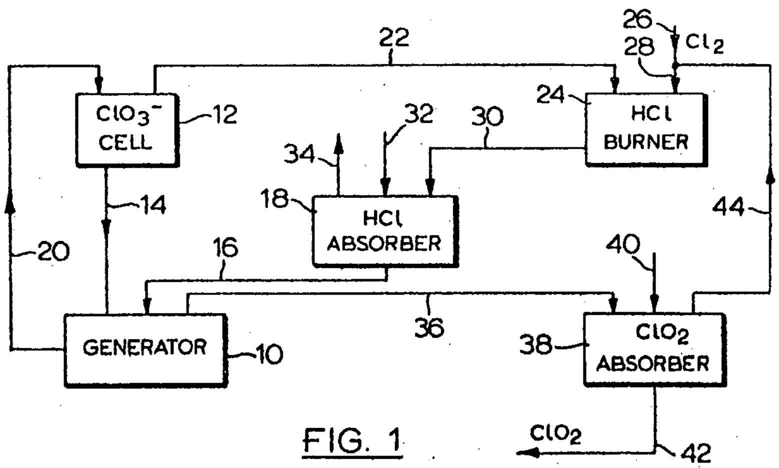

FIG. 1

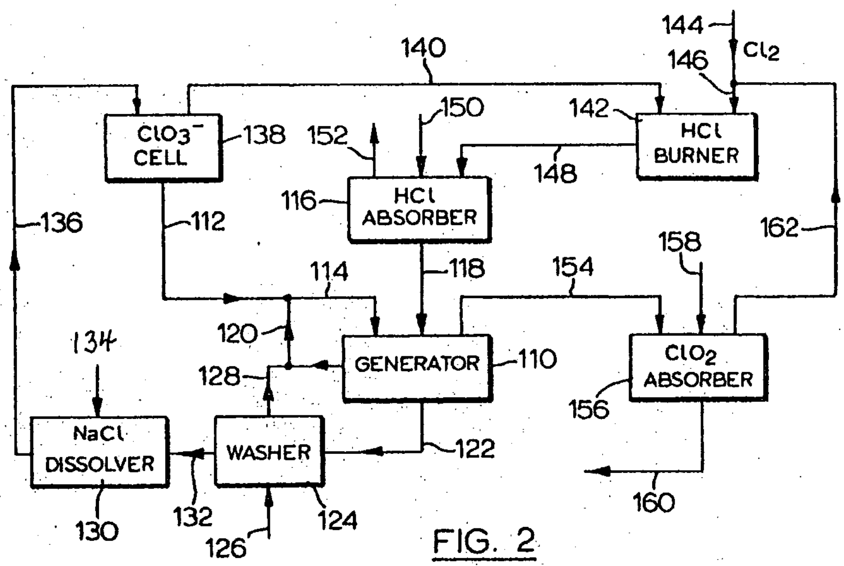

FIG. 2

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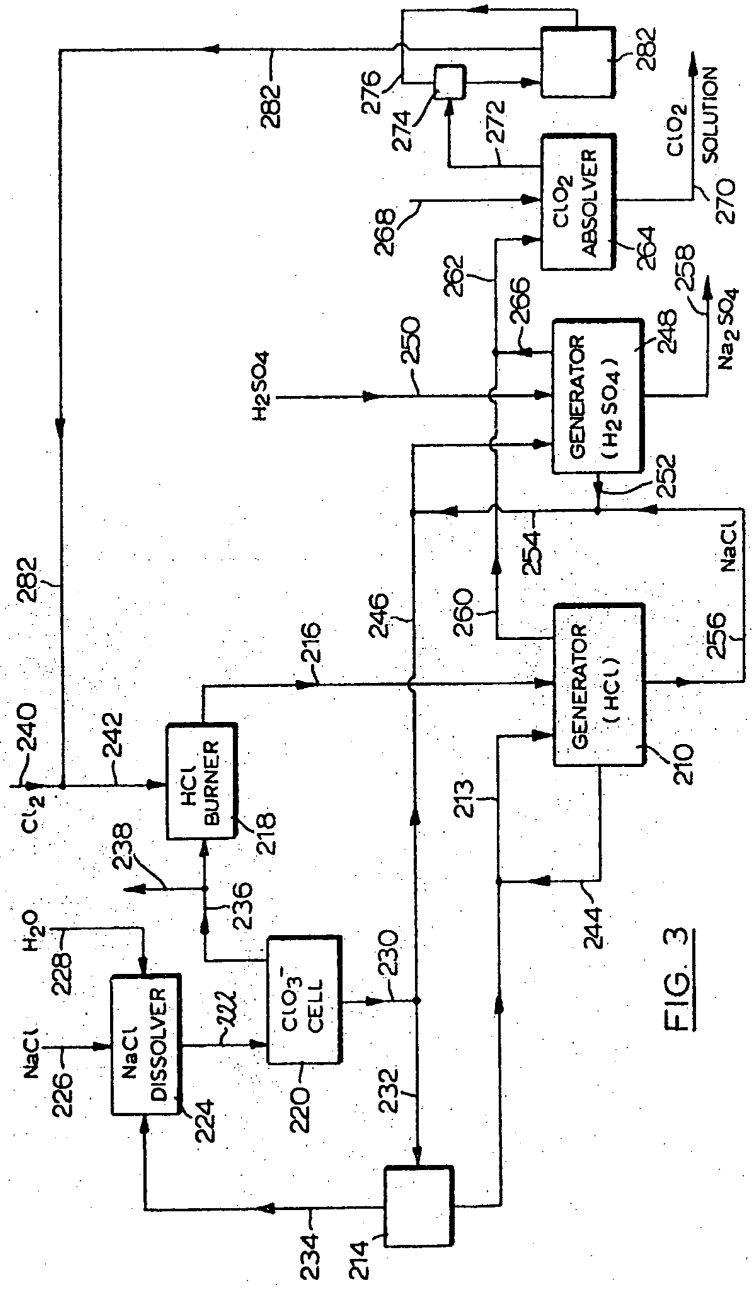

FIG. 3